"AN EVALUATION OF THREE NEUTRON ACTIVATION ANALYSIS METHODS FOR MERCURY IN COAL"

Jack N. Weaver, Nuclear Engineering Department, N.C. State University, Raleigh, N.C.
Darryl J. von Lehmden, Environmental Protection Agency, Division of Atmospheric Surveillance, Source Sample and Fuels Analysis Branch, Research Triangle Park, N.C.

INTRODUCTION

Due to the rapid growth in heavy industry in the United States, man has displaced many chemical elements from their natural environment and has poured them back into his daily environment. In order to determine the extent chemical elements in process raw materials and fuels contribute to the environment, the Environmental Protection Agency has initiated a program of analysis for a variety of elements including mercury, beryllium, cadmium, arsenic, vanadium, manganese, nickel, antimony, chromium, zinc, copper, lead, selenium, boron, fluorine, lithium, silver and tin. To conduct this analysis program on raw materials and fuels has required the evaluation of analytical techniques available for chemical elements in trace quantities, especially for mercury.

In just such an endeavor, the Environmental Protection Agency (EPA) in conjunction with the Nuclear Engineering Department of North Carolina State University (NCSU) evaluated neutron activation analysis (NAA) of mercury in a round-robin series of coal samples from the U.S. Bureau of Mines. This round-robin series was selected for two reasons. These were (1) extensive and careful efforts had gone into selecting and preparing the coal samples; and (2) the many laboratories (both atomic absorption and neutron activation analysis) participating in the series provided an excellent check on the accuracy of the results.

To completely cover the ranges of mercury expected in the coal samples, three types or variations of NAA were tried. These were:

1. Instrumental NAA using a 3×10^{13} n/cm^2-sec irradiation and counting on a large (Lithium drifted germanium) Ge(Li) co-axial detector.
2. A 3×10^{13} n/cm^2-sec irradiation followed by radiochemistry and counting on a 3" x 3" NaI detector.
3. A 3×10^{13} n/cm^2-sec irradiation and counting on a newly developed 10 mm Ge(Li) Low Energy Photon Detector.

TABLE #1

Geological Background of Coal Samples

Sample #	Geological Location	Mining Process
DRB-A	Belmont Co., Ohio	Strip - raw
DRB-B	Harrison Co., Ohio	Deep - raw
DRB-C	Jefferson Co., Ohio	Strip - washed
DRB-D	Kanawha Co., W. Va.	Deep - washed
DRB-E	Washington Co., Pa.	Deep - washed
G-1	Clay Co., Indiana	Deep - washed
P-1	Muhlenberg Co., Ky.	Raw
P-2	Rosebud Co., Mont.	Raw
P-3	Henry Co., Mo.	Washed - raw
P-4	Montrose Co., Colo.	Raw
P-5	Navajo Co., Ariz.	Raw

EXPERIMENTAL

Sampling and Preparation for Irradiation

Fresh samples of coal representative of the mines listed in Table I were obtained and sample preparation was as follows:

1. Each plastic bottle was washed with a 2-1 mixture of concentrated nitric acid and hydrochloric acids, rinsed first with distilled water and then with acetone. The bottles were air dried and capped.

2. Coals were sampled, crushed to minus 60 mesh, divided equally and placed in the cleaned sample bottles.

From these coal samples, three sets of samples of each were carefully transferred to pre-cleaned low mercury content poly-irradiation vials. After weighing, these were heat sealed along with sets of carefully calibrated 1 and 5 microgram mercury standards. These samples provided the necessary number to perform duplicate analyses with each of the three techniques.

Nuclear Parameters

Weight of coal: 0.25 to 0.50 grams

Reactor neutron flux: 3×10^{13} n/cm^2-sec

Irradiation time: 4 hours

Decay times: Approximately 4 days for Technique 1 and 3 and approximately 7 days for Technique 2.

Technique #1
Radiochemistry and Counting on a 3" x 3" NaI (Well-Type) Detector

1. Approximately 24 hours after irradiation, the poly vial containing approximately 0.5 gram of coal dust was opened and the contents were completely transferred to a clean distillation flask.

2. Using 100 ug of mercuric oxide as a carrier and 8 to 9 ml of fuming H_2SO_4 for digestion, the solution was mixed, then heated.

3. Next, fuming nitric acid was added. The addition of HNO_3 was repeated until charring was complete.

4. A small amount of water and potassium bisulfate was added to drive off the nitric acid and nitric fumes.

5. After appropriate cooling and transfer of the contents to a 300 ml calibrated beaker, the normality was adjusted to approximately 0.2 N and a standard dithiozone extraction procedure was used to remove the mercury.

6. The final extraction (approx. 50 ml) containing the mercury was poured into a 150 cc wide bottom plastic bottle for counting on a 3" x 3" (well-type) NaI detector.

7. The 0.07 MeV photopeak of Hg-197 was utilized for the classic method of data reduction and statistical evaluation.

8. Figures #1 and 2 illustrate the typical gamma spectrum of this extraction and the mercury standard respectively.

Technique #2
Instrumental NAA Using a 36 cc Ge(Li) Detector Coupled to a 4096 Nuclear Data Multichannel Analyzer

1. After a 7-day decay, the poly irradiation container was opened and the coal powder was transferred to a flat bottom plastic 100 ml bottle for counting. The bottle was tapped to provide a uniform spread of the powder over the bottle bottom.

2. Each sample was counted for 30 minutes on a 36 cc co-axial Ge(Li) detector coupled to a 4096 Nuclear Data Multichannel Analyzer.

3. Data reduction was performed using the classic method and the 0.07 MeV x-ray of Hg-197.

4. Figures #3 and 4 illustrate the spectra obtained with this counting system for unknown and standard respectively.

Technique #3
Instrumental NAA Using a 10 mm Ortec Low Energy Photon Detector Coupled to a RIDL 400 Channel Analyzer

1. After a 4-day decay, the poly irradiation container was opened and the coal powder was transferred to a flat bottom plastic 15 ml bottle for counting. The bottle was tapped gently to provide a uniform spread of the powder over the bottle bottom, thus insuring the geometry over the 10 mm surface of the detector window.

2. Each sample was counted for 30 minutes on a 10 mm Ge(Li) Ortec Low Energy Photon Detector coupled to a 400 channel RIDL analyzer.

3. Data reduction was performed using the classic method and the 77.97 KeV x-ray of Hg-197.

4. Figures #5 and 6 illustrate the spectra obtained with this counting system for unknown and standard respectively.

RESULTS

The results of all three NAA techniques plus the average results of the same samples analyzed by 8 other laboratories participating in the coal round-robin analysis are shown in Table 2. The other laboratory techniques were flameless atomic absorption and neutron activation analysis with radio-chemistry.

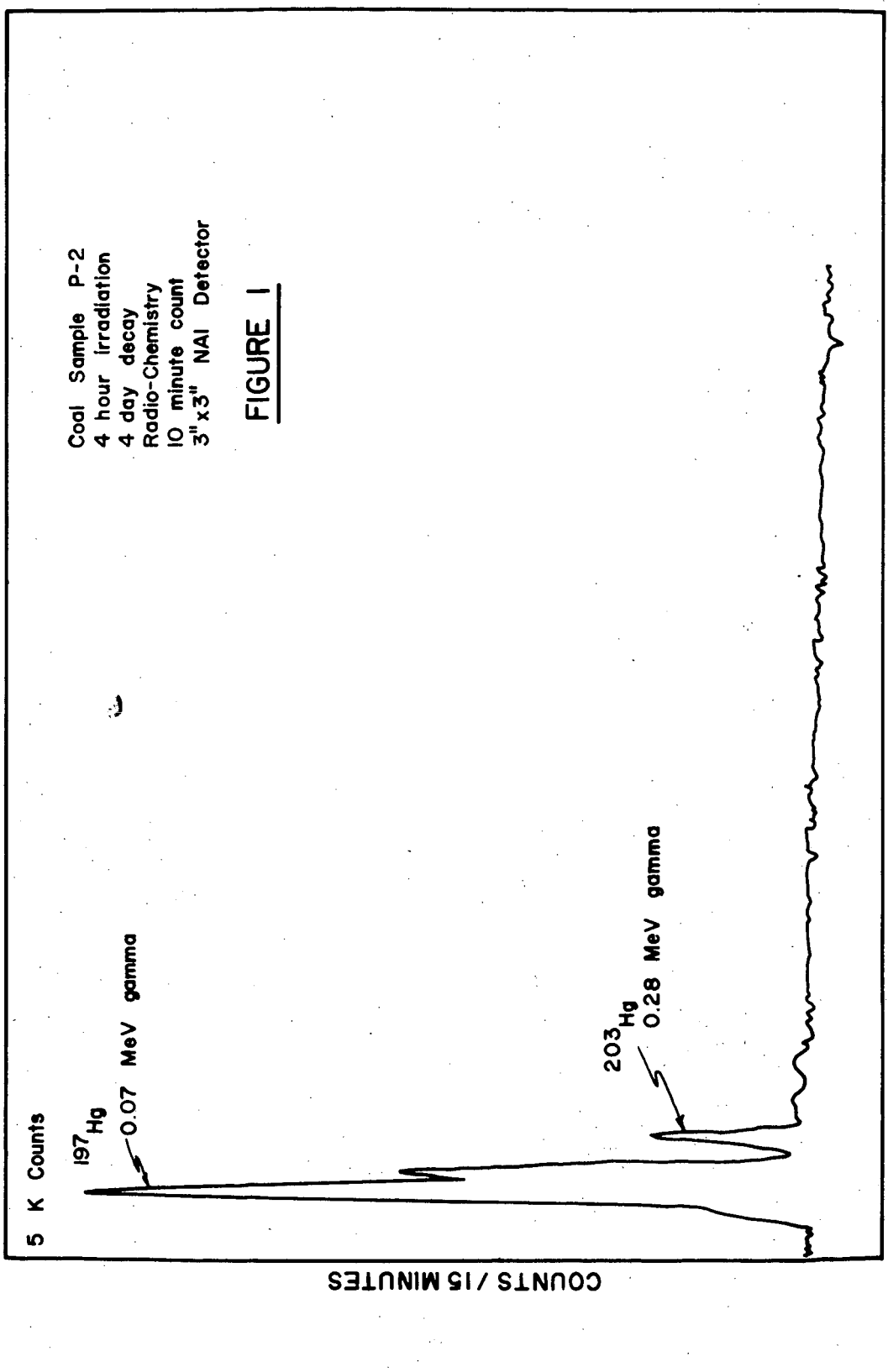

Coal Sample P-2
4 hour irradiation
4 day decay
Radio-Chemistry
10 minute count
3" x3" NAI Detector
5 K Counts
197Hg
0.07 MeV gamma
203Hg
0.28 MeV gamma
COUNTS / 15 MINUTES
GAMMA ENERGY

FIGURE 1

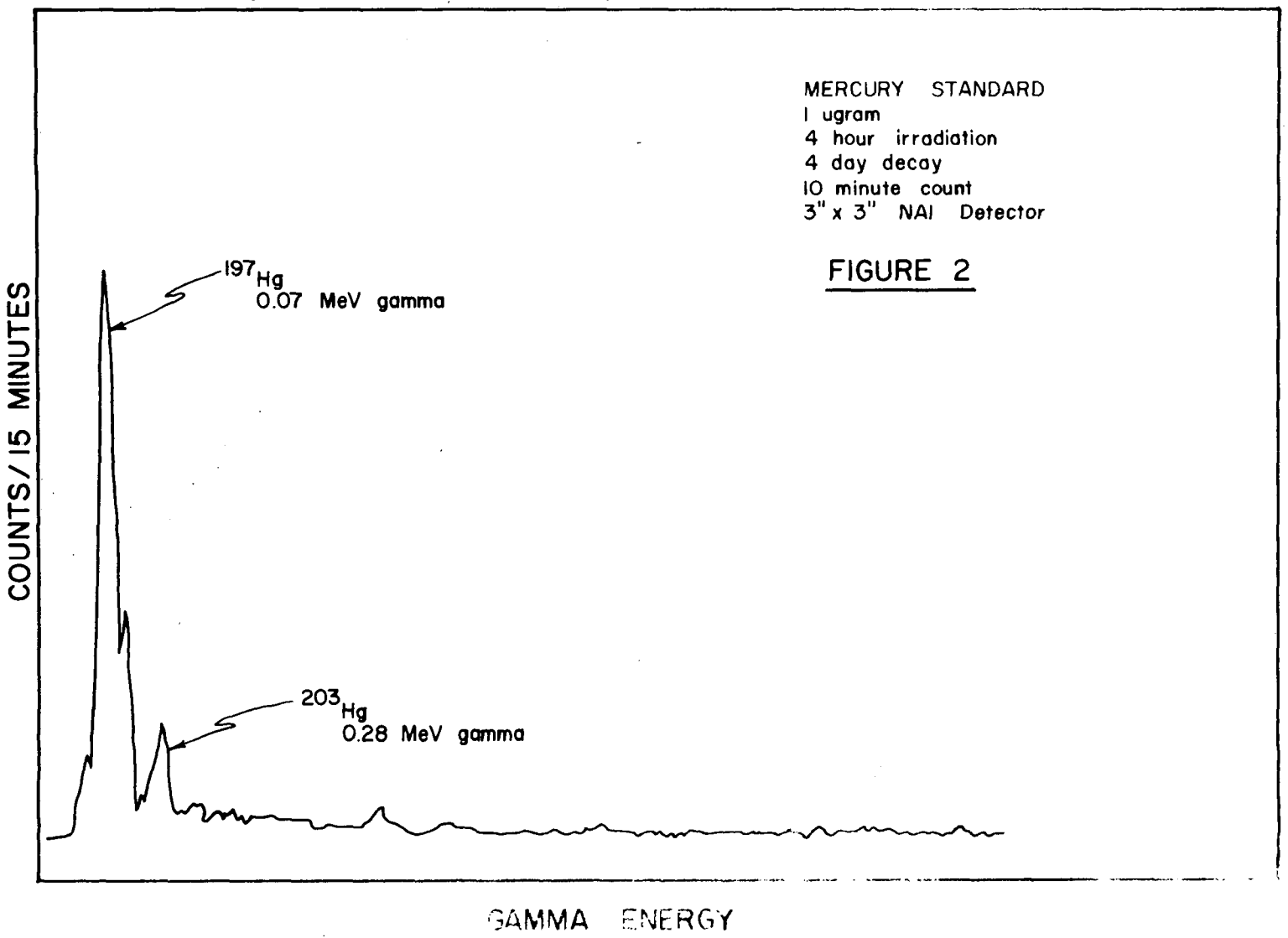

MERCURY STANDARD
1 ugram
4 hour irradiation
4 day decay
10 minute count
3" x 3" NAI Detector
197Hg
0.07 MeV gamma
203Hg
0.28 MeV gamma
COUNTS/15 MINUTES
GAMMA ENERGY

FIGURE 2

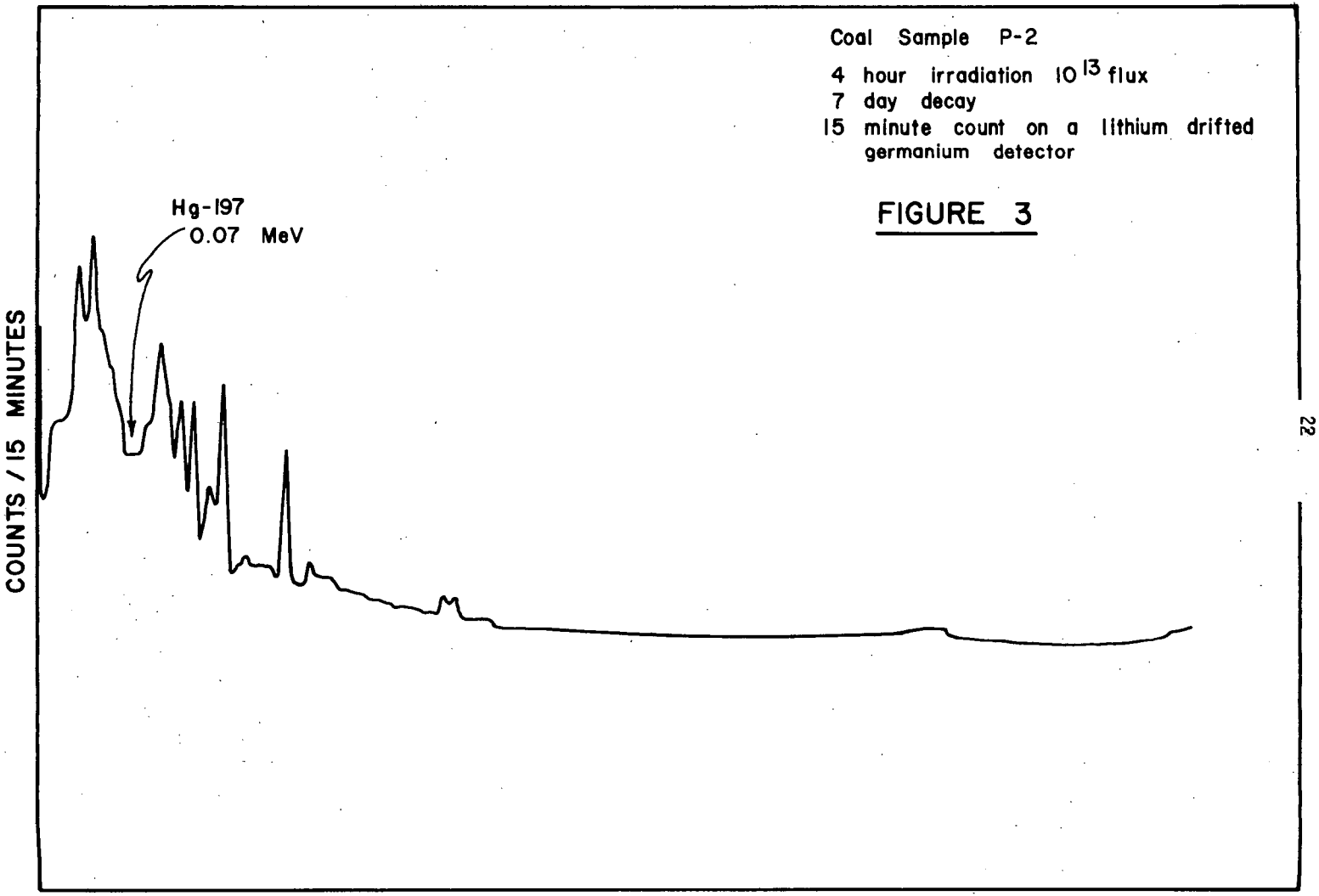

Coal Sample P-2
4 hour irradiation 10^{13} flux
7 day decay
15 minute count on a lithium drifted germanium detector
Hg-197
0.07 MeV
COUNTS / 15 MINUTES
GAMMA ENERGY in MeV

FIGURE 3

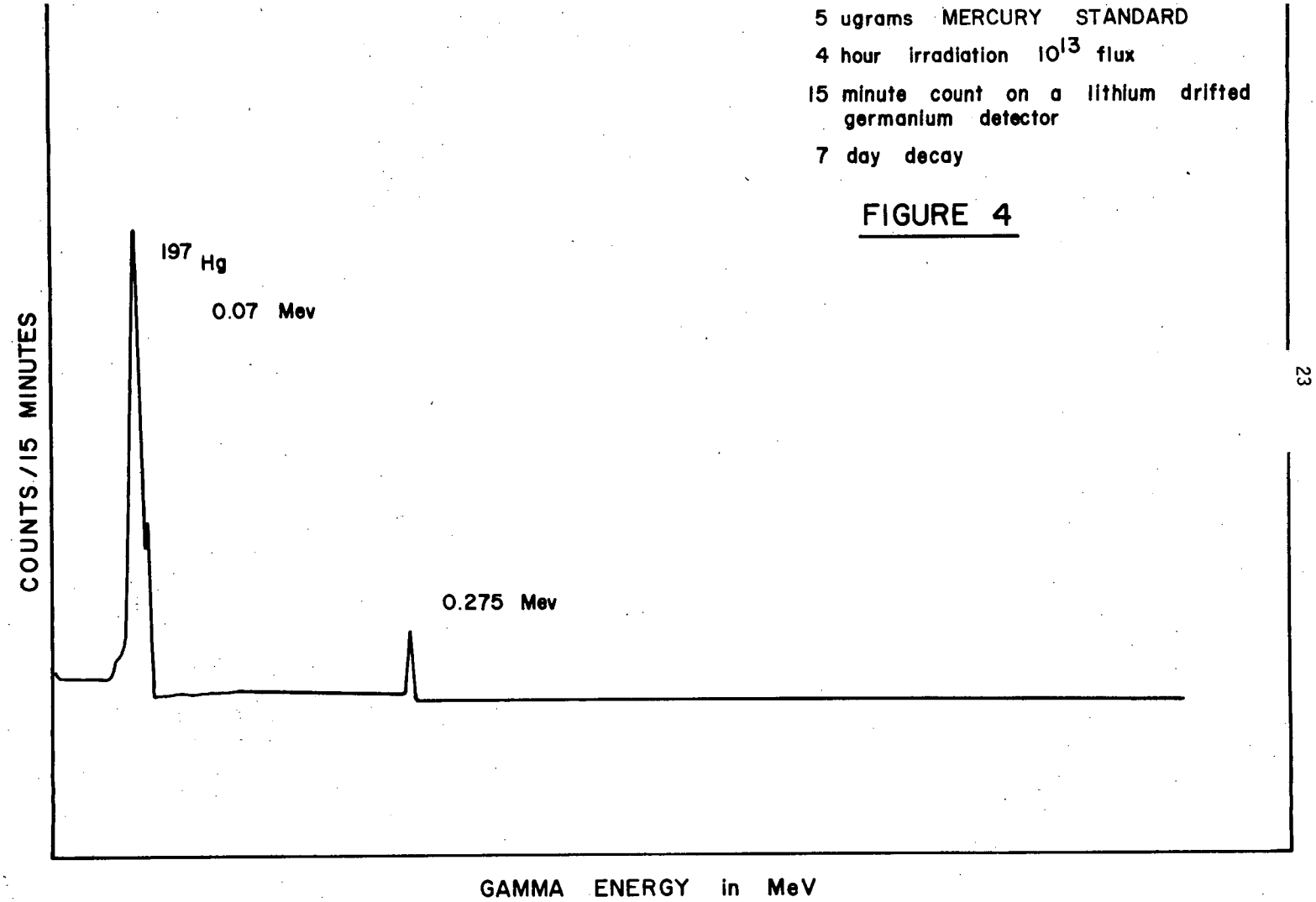
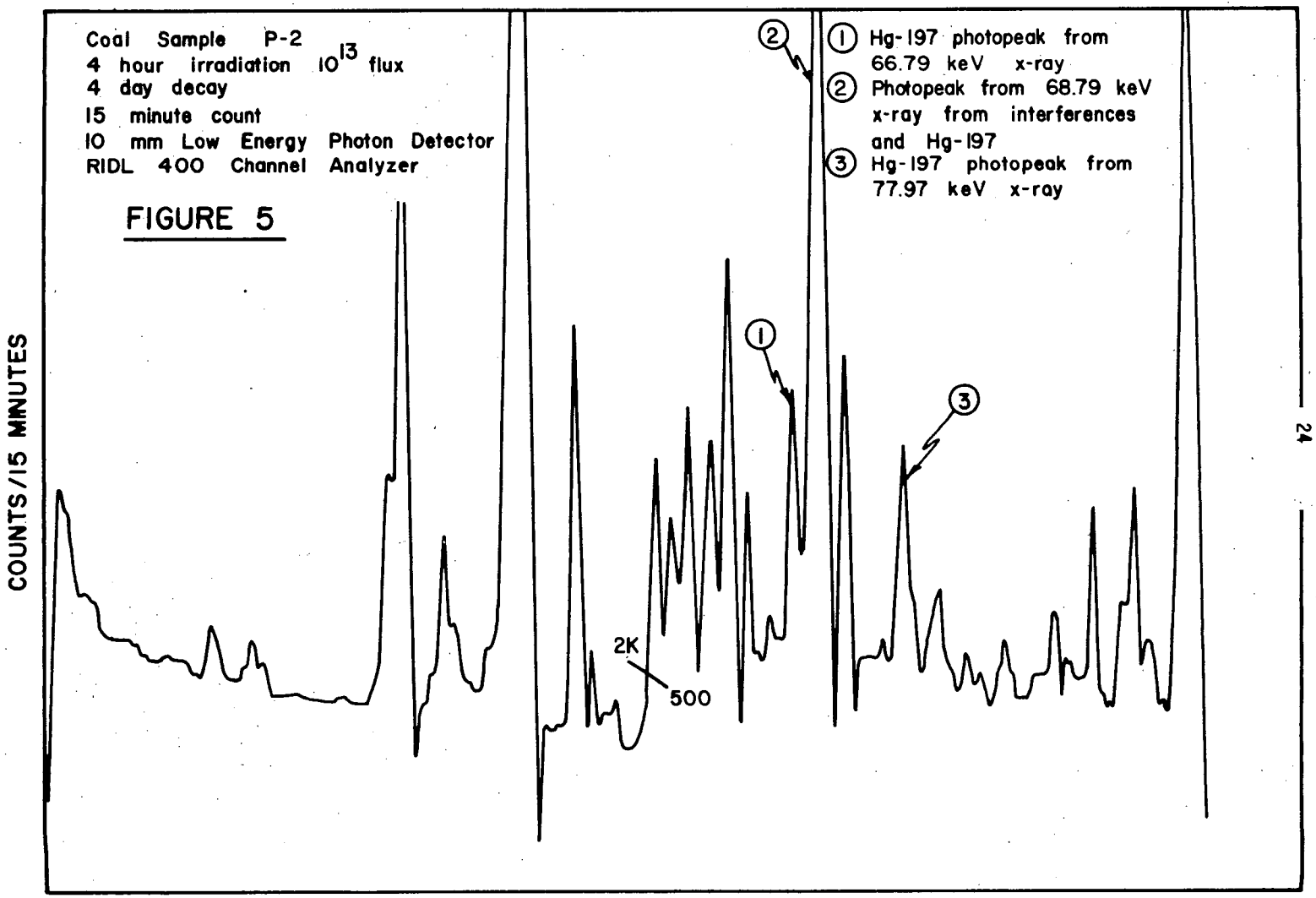

5 ugrams MERCURY STANDARD
4 hour irradiation 10^{13} flux
15 minute count on a lithium drifted germanium detector
7 day decay
197 Hg
0.07 Mev
0.275 Mev
COUNTS/15 MINUTES
GAMMA ENERGY in MeV

FIGURE 4


Coal Sample P-2
4 hour irradiation 10^{13} flux
4 day decay
15 minute count
10 mm Low Energy Photon Detector
RIDL 400 Channel Analyzer
FIGURE 5
① Hg-197 photopeak from 66.79 keV x-ray
② Photopeak from 68.79 keV x-ray from interferences and Hg-197
③ Hg-197 photopeak from 77.97 keV x-ray
COUNTS/15 MINUTES
2K
500

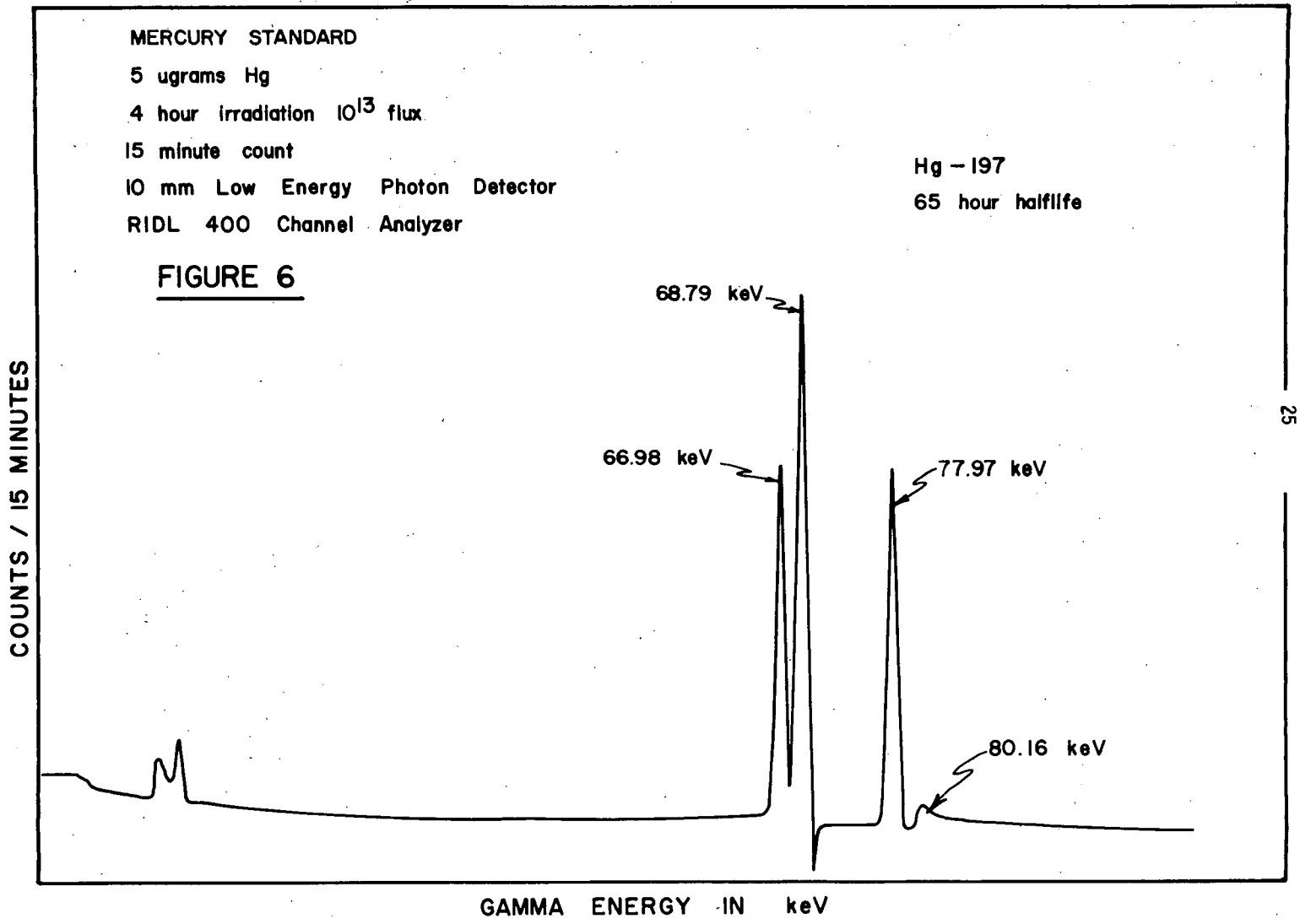

MERCURY STANDARD
5 ugrams Hg
4 hour irradiation 10^{13} flux
15 minute count
10 mm Low Energy Photon Detector
RIDL 400 Channel Analyzer
Hg – 197
65 hour halflife
68.79 keV
66.98 keV
77.97 keV
80.16 keV
COUNTS / 15 MINUTES
GAMMA ENERGY IN keV

FIGURE 6

TABLE #2

Total Mercury Levels in Coal

(ppm)

Sample Description	Radio Chemistry and NaI	Instrumental and 36 cc Ge(Li)	Instrumental & Low Energy Photon	Average of Laboratories Using NAA and AAA
DRB-A	0.130	< 0.37	0.16	0.14
DRB-B	0.380	0.17	0.43	0.44
DRB-C	0.230	0.54	0.27	0.24
DRB-D	0.069	0.19	0.09	0.07
DRB-E	0.100	0.16	0.12	0.13
G-1	0.086	0.15	0.10	0.07
P-1	0.170	0.55	0.17	0.17
P-2	0.057	< 0.42	0.07	0.06
P-3	0.150	0.48	0.17	0.15
P-4	0.035	0.43	0.07	0.05
P-5	0.058	< 0.34	0.08	0.06

DISCUSSION OF RESULTS

As can be seen from the description of each technique, the three methods were kept as simple to perform as possible since we were striving to achieve a rapid, accurate procedure for routine coal analysis. This simplicity was developed in conjunction with thorough efforts to maintain duplicate conditions for both standards and unknowns. In evaluating the three NAA techniques for mercury analysis in coal, the following conclusions were reached:

Technique #1 involving NAA and radiochemistry proved to be a very reliable method of analysis with close agreement of results to other laboratory results. However, the total number of samples that can be analyzed is limited by the restriction of having to dissolve the coal and perform time-consuming radiochemistry. A great deal of technician contact is required in the chemical separation, and the visual interpretation of the different steps of the separation could lead to recovery errors if on a routine basis. A significant amount of glassware is required plus the obvious limitation of hood space versus number of separation units that can occupy that space. Hence, the main drawbacks to radio-chemical separation are the tie-up of equipment and manpower with a limited analysis rate, plus possible recovery errors.

Technique #2 using a large coaxial Ge(Li) detector for instrumental NAA proves to be inadequate as the results in Table 2 illustrate. In this matrix and at these sub-microgram levels, interferences from other elements prevent an accurate analysis using the 0.07 MeV gamma ray of Hg-197. Similar work by McLain and Leddicotte [1] at Georgia Tech confirm these results in that large volume Ge(Li) detectors do not possess the required resolution in the x-ray region of the energy spectrum. Note the poor energy curve for mercury in Figure #3.

Technique #3 using the Low Energy Photon Ge(Li) detector (LEPD) for instrumental NAA by far appears to offer the most promise for future analysis of environmental matrices such as coal, fuel oils, air particulates, etc. The fact that all that is required is a 4-10 hour irradiation at a flux of 10^{13} neutrons/cm^2-sec, plus a 24-72 hour decay, and a 20 minute count on a 16 mm LEPD (this work was performed using a 10 mm detector width, but the 16 mm is preferred due to the increase in sensitivity versus cost) means that highly accurate, inexpensive, and instrumental NAA can be performed at a rapid analysis rate.

The main factor behind the LEPD's usefulness is that of its extremely fine resolution (220 eV at 55 KeV which in this case clearly defines Hg-197's 66.98, 68.79, 80.16 KeV x-rays and 77.97 KeV gamma ray. Hence, even with possible interferences, the choice of 1 of 3 or 4 photopeaks allows one to accurately perform the quantitative analysis. When photopeak count rate ratios do not compare those of the Hg-197 standard, a half-life determination based on a second count can be used to choose the photopeak for quantitative analysis.

SUMMARY

An evaluation of three NAA techniques for mercury analysis in coal has been presented with special emphasis given to the use of a 16 mm Low Energy Photon Ge(Li) Detector for rapid instrumental NAA.

Preliminary results show the possibility that many other elements with nuclides having low energy x-rays can easily be analyzed in coal using the LEPD gamma detector.

1/ D. M. Walker, M. E. McLain, and G. W. Leddicotte, "Semiconductor Detector Optimization for Trace Mercury Analysis in Environmental Samples", Georgia Institute of Technology, Atlanta, Georgia